DETECTION OF LANDFILL LEACHATE IN GROUNDWATER AND SURFACE WATER USING **FLUORESCENT INDICATORS**

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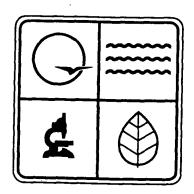
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INTRODUCTION

This study was conducted by the Missouri Department of Natural Resources through a grant provided by the US Environmental Protection Agency to evaluate the impacts of the Great Flood of 1993 on Missouri landfills. The purpose of this portion of the overall project was to develop fluorometric methods to distinguish landfill leachate and leachate-impacted water from unaffected waters.

BACKGROUND

As leachate produced by the degradation of solid waste migrates through natural materials, its characteristics are changed by a variety of physical, chemical and biochemical processes.

Concentrations of specific chemical constituents, which are found to be elevated near the source, are reduced. Bioremediation, volatilization, and simple dilution are all factors that hinder differentiation of leachate from background waters. Since leachate normally contains only trace levels of many different constituents, it is often cost-prohibitive to analyze water samples for more than a small fraction of the actual constituents which may (or may not) be present.

Regulatory agencies typically rely on monitoring for constituents which have well-established health-based standards. Often detection limits are set at such a standard because of the increased cost of analyzing for lower detection limits. While this approach is one way to monitor water at a reasonable cost, it is not always effective at detecting contaminants. Nor does this approach always help determine which water supplies are at risk. Low concentrations of constituents indicative of leachate may not be detected that could otherwise alert users to potential dangers.

Leachate exhibits relatively strong fluorescence in the range of 250 to 450 nanometers (nm). The

premise upon which this study is based is that some fluorescent byproducts of the degradation of solid waste may be useful in detecting leachate in the environment. Other sources of organic contaminants (such as domestic sewage and wood waste leachate) may be detectable in the same way. The focus of this study was to determine the effectiveness of specific techniques in identifying fluorescent indicators of landfill leachate in raw (untreated) surface water and groundwater. No attempt was made to identify specific fluorescent constituents. The intent was to determine a gross fluorescence signature of leachate and diluted leachate with an overall goal of developing inexpensive fluorescence techniques for preliminary identification of leachate-affected waters. By prioritizing sampling points for additional sampling (via conventional analytical methods) a more complete depiction of potentially contaminated waters could be produced.

This study was divided into two parts. The first involved the initial fluorescence characterization of leachate and leachate-affected waters from a single landfill. Two scanning fluorescence spectrometer analysis methods were developed during this phase. One method involved synchonously scanning the excitation and emission spectra of raw water samples. The second method involved three-dimensional contouring of the fluorescence of raw water samples. Both methods were used to compare leachate-affected water to background waters that were not suspected of being affected by leachate.

The second phase involved the testing of fluorescence methods developed in the first phase. Samples were collected from six landfills in conjunction with split samples for analysis by conventional wet chemistry techniques. The intent of this phase was to compare the fluorescent classification of waters with more standardized methods in order to determine the effectiveness of the fluorescence methods.

TWO DIMENSIONAL FLUORESCENCE METHODS

Fluorescence spectrometers equipped for synchronous scanning have been used for years to differentiate fluorescent materials such as oils in the environment (Fels, 1997; Frank, 1973;

Kerfoot, 1981). Synchronous scanning provides maximum sensitivity by reducing interference of scattered light which passes directly through the instrument's optics using single scan or fixed filter techniques. Similar equipment and methodologies have been used for detection of fluorescent tracers in geohydrologic studies and waste-disposal investigations (Duley, 1986). Pharr and others (1992) used synchronous fluorescence analysis to "fingerprint" petroleum contamination in soil and groundwater. Pullin and Cabaniss (1995) have used the technique to characterize humic substances. Cabaniss, through personal communication in 1997, shared that he has used similar methods for fingerprinting surface waters.

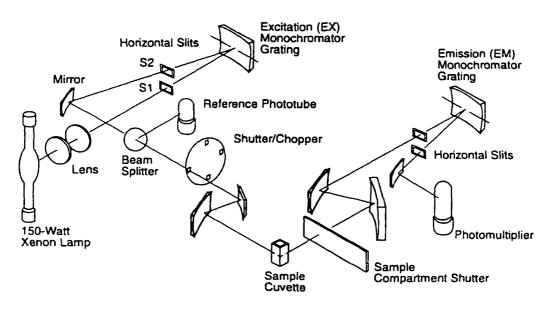
Techniques similar to those of the authors above were used in this effort to fingerprint leachate in water. Samples of raw leachate were collected from four wells installed in waste at Renfro's Landfill in Stone County, Missouri. Samples were collected from the wells, using polyethylene bailers, placed in disposable polypropylene cups with polyethylene caps, transported on ice, out of sunlight, and analyzed within 48 hours of collection. Additional samples were collected from springs, surface-water points located near the landfill and a tank, which receives water from a leachate collection system of questionable effectiveness, to compare potentially-impacted waters with the raw leachate. A limited number of domestic sewage and sawdust leachate samples were also analyzed for comparison of the fluorescence characteristics of those waste streams. Surface water samples were collected, transported and analyzed in the same manner as well water samples, except bailers were not used.

Most fluorescence spectrophotomers operate similarly. Each instrument has a light source (usually a xenon lamp) to excite fluorescent materials. Light from the xenon lamp passes through a scanning monochromator to provide an excitation light beam of a specific band of wavelengths that passes through the sample. If fluorescence is induced, light of a longer wavelength is emitted from the sample that passes through a second scanning monochromator, which allows only a selective band of wavelengths of light to pass. The light that passes through the optic system is measured at a photomultiplier tube. A schematic of the optics of the instrument used for fluorescent analysis in this particular study is shown in Figure 1.

Analysis of samples involved synchronous scanning of raw water samples. Separation between

excitation and emission monochromators was set at 20 nanometers (nm). Using this method, both monochromators are varied so that the wavelengths of light passing through them are increased at the same scan rate to maintain a set wavelength separation of 20 nm. The 20 nm separation normally does not produce the largest peaks but does produce spectra that allow differentiation of fluorescent organics in wastewater. The resultant output is an XY graph of excitation wavelength on the X axis versus fluorescent intensity on the Y axis that represents the relative amounts of light that are emitted from the sample through fluorescence as both monochromators are varied continuously.

FIGURE 1
Schematic of Optical Module for Hitachi F-4500 Fluorescence Spectrometer



RESULTS

Initial results of two-dimensional scans showed that the leachate samples analyzed display strong fluorescence. In fact, raw leachate normally requires dilution on the order of about one order of magnitude to overcome inner-filter effects that cause an apparent reduction of fluorescence, especially at shorter wavelengths. Fluorescence of diluted leachate showed remarkable similarities to the fluorescence of water from springs suspected to be impacted by leachate and water collected from the landfill's leachate collection system (which was suspected of being

disconnected from the landfill). Just as significantly, remarkable differences were observed between the fluorescence of diluted leachate and background water samples.

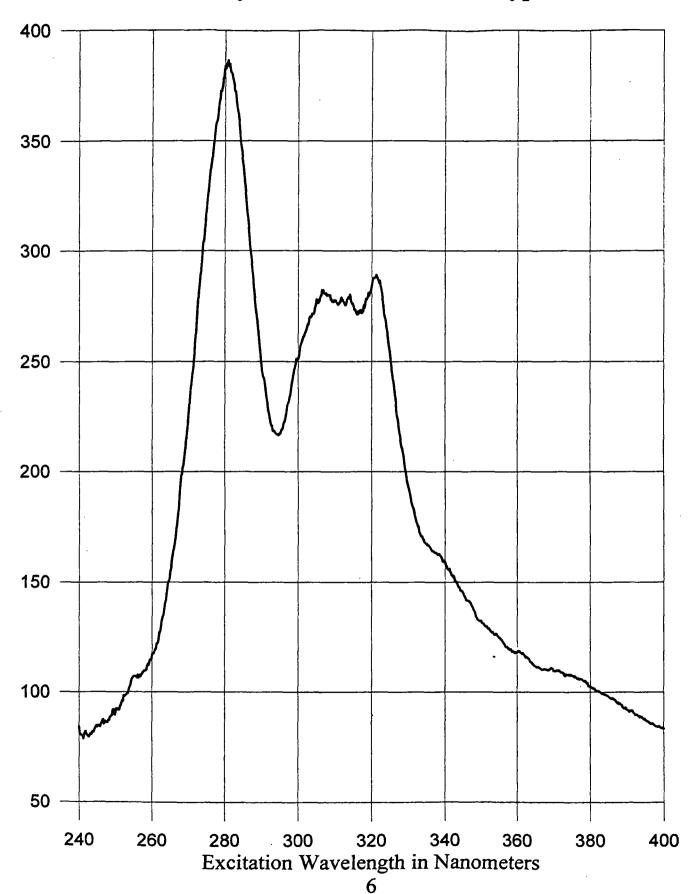
Leachate typically displays a large peak at approximately 280 nm excitation wavelength with smaller, less distinct peaks between 300 and 350 nm (Figure 2). The domestic sewage analyzed typically shows the large peak at about 280 nm but lacked the comparable peaks at higher wavelengths. The sawdust leachate analyzed also displayed some spectral differences between it, other organic wastes, and background or unimpacted water (Figures 3-5). Distilled water and unimpacted water typically display only minor amounts of fluorescence at excitation wavelengths below 280 nm. These small peaks may be more intense in background water than leachate because inner-filter effects, which reduce fluorescence at lower wavelengths in impacted water, are greatly reduced in background water.

THREE DIMENSIONAL FLUORESCENCE TECHNIQUES

A contour plot of fluorescence may be constructed by combining multiple scans of either excitation or emission wavelength data with corresponding small offsets in the alternative monochromator. For example, one may conduct an emission scan of a given portion of the spectrum with the excitation monochromator fixed at a set wavelength. The fixed wavelength of the excitation monochromator is then increased slightly (a few nanometers) and the emission scan is repeated. This process is repeated until all specified portions of both excitation and emission spectrums have been covered. The fluorescent intensities obtained are plotted on the Z wavelengths axis with the resulting contour superimposed on an X-Y graph of the excitation versus emission (Figure 6).

The three dimensional fluorescence technique has been used to contour and compare different commercial motor oils by Retzik and Froehlich (1992). Generally, the technique has not gained wide acceptance outside of the research community because most fluorescence spectrometers on the market are not capable of collecting and processing data rapidly enough to economically analyze large portions of the spectrum of multiple samples. Recent advances in the design of

Figure 2
20 Nanometer Synchronous Scan of a Typical Leachate



Kelanve intensity

Figure 3

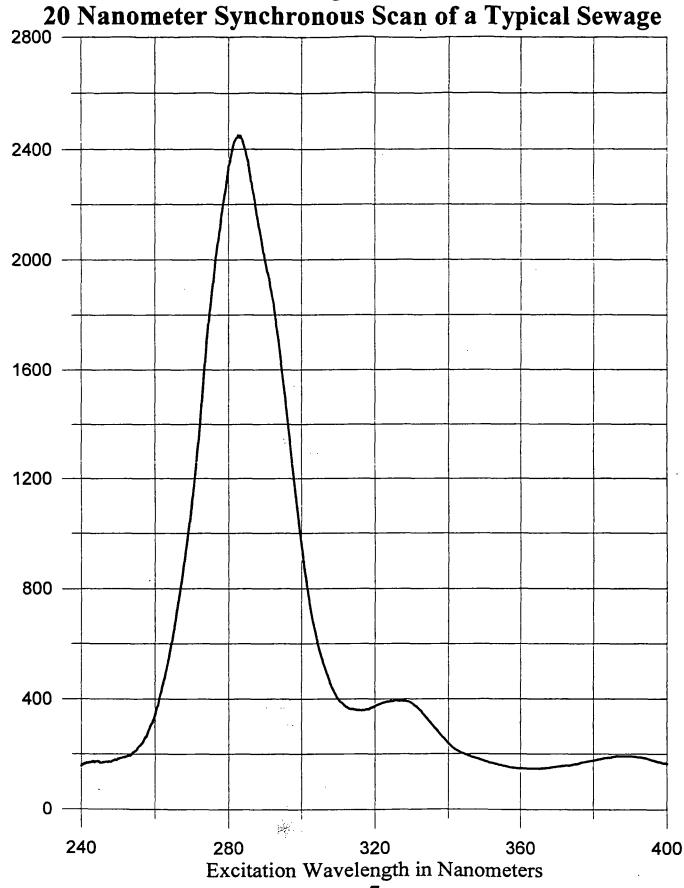


Figure 4
20 Nanometer Synchronous Scan of a Typical Sawmill Leachate

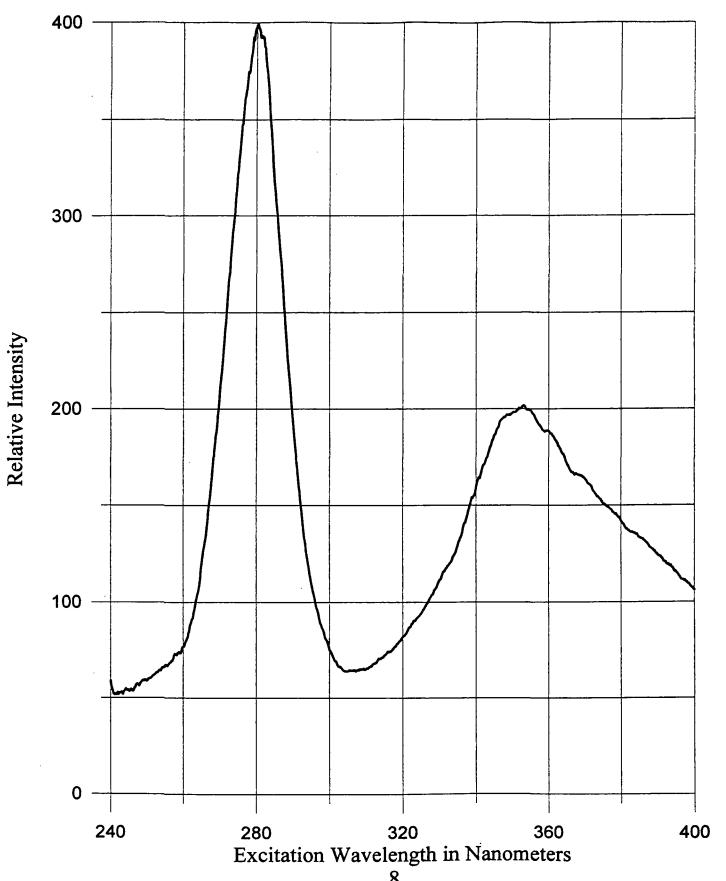


Figure 5
20 Nanometer Synchronous Scan of Background Water

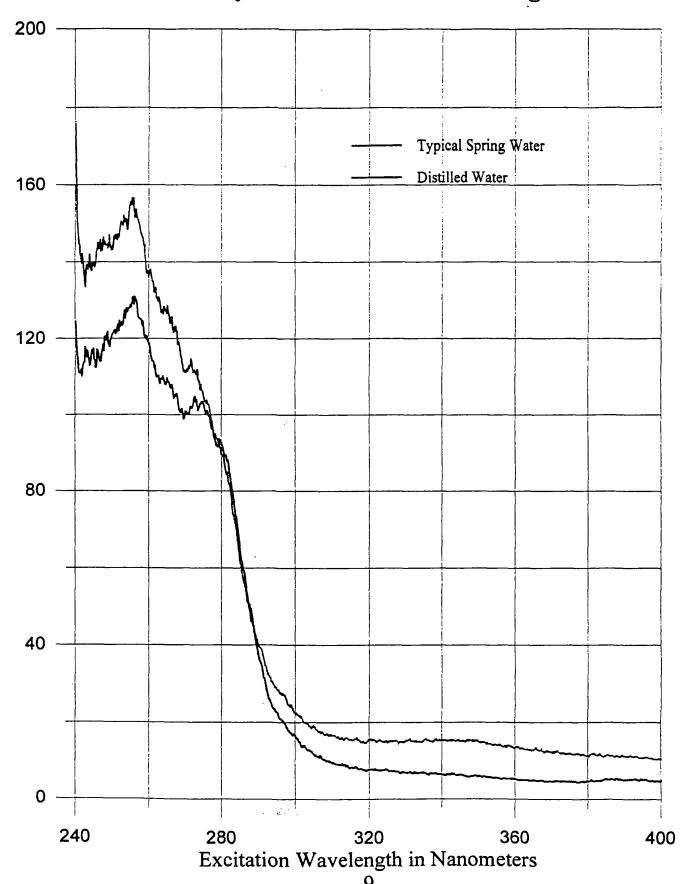
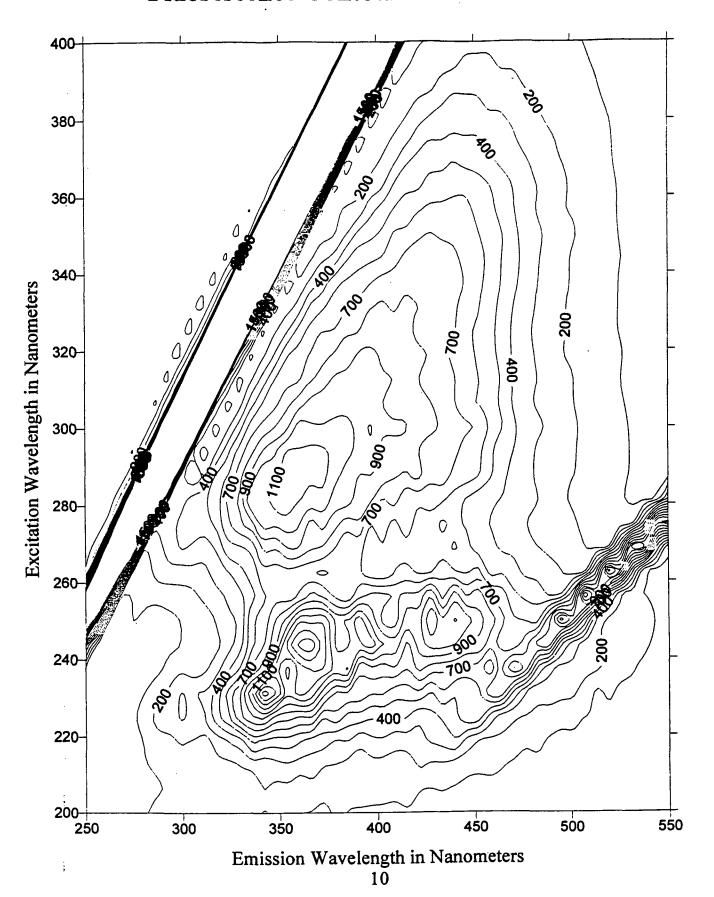


Figure 6
Fluorescence Contour Plot of a Leachate



fluorescence spectrophotometers allow rapid data collection and processing. The data shown in Figure 6 required less than two minutes to collect at a scan speed of 30,000 nm/minute (nm/min). At a scan speed of 240 nm/min, which is more typical of this type of instrument, this analysis would have required more than two hours.

Fluorescence contouring data for the leachate fingerprinting were collected with a Hitachi model F-4500, which is capable of scan speeds up to 30,000 nm/min. As a practical note, it was observed that scan speeds up to 30,000 nm/min were useful for quick analyses, but lower speeds yielded better resolution. Export of data to a computer contouring program that is capable of smoothing contours, significantly reduces noise in plots of rapidly acquired spectral data, yet preserves the characteristic spectral patterns of specific waste types.

Preliminary scans showed that the bulk of fluorescence of leachate samples fell in the range of 200 to 400 nm excitation and 250 to 550 nm emission. Analyses were focused on these ranges.

Specific examples of fluorescence contouring of water samples are shown in Figures 7 through 11. The contoured spectral data generally shows peaks clustered in four spectral zones: Zone A-300 to 400 nm excitation, Zone B- 260 to 300 nm excitation, Zone C- 200 to 260 nm excitation and 280 to 360 nm emission, and Zone D- 200 to 260 nm excitation and 360 to 550 nm emission (Figure 12). Leachate and sewage may exhibit peaks in all four zones. These peaks were typically intense but broad with respect to both excitation and emission wavelengths. Fluorescence intensity was useful in distinguishing impacted water from non-impacted water. Specific peak locations and intensities in leachate samples varied due to complications such as fluctuating pH and differing concentrations of fluorescent constituents in the sample analyzed. In spite of this complication, the overall intensity of peaks, normalized to a 10 part per billion Rhodamine WT standard, generally displayed a linear trend when plotted logarithmically versus concentration of leachate (Figure 13).

Figure 7
Fluorescence Contour Plot of Distilled Water

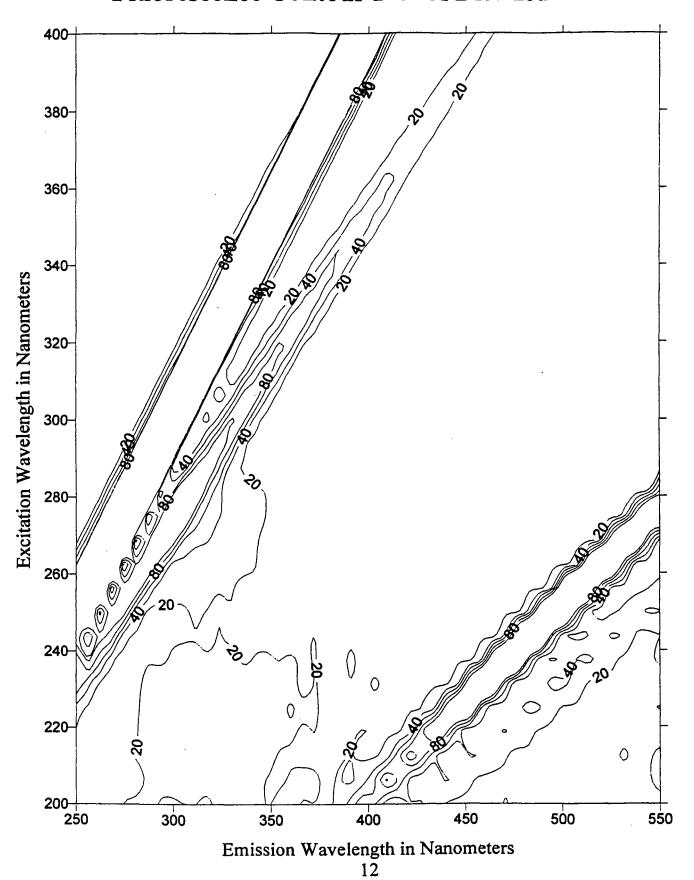


Figure 8
•Fluorescence Contour Plot of Background Water

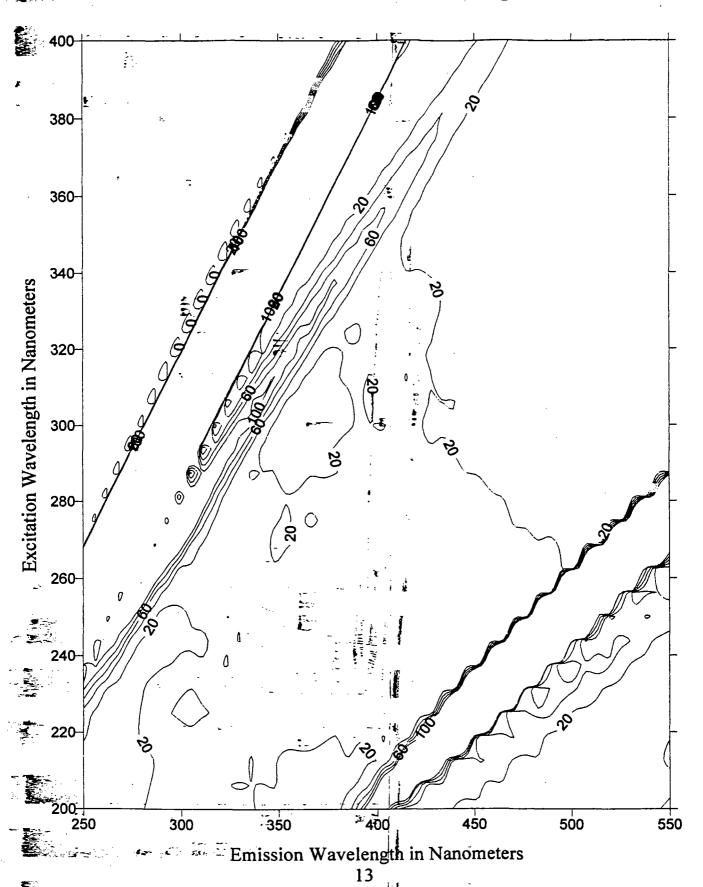


Figure 9
Fluorescence Contour Plot of a Leachate Impacted Spring

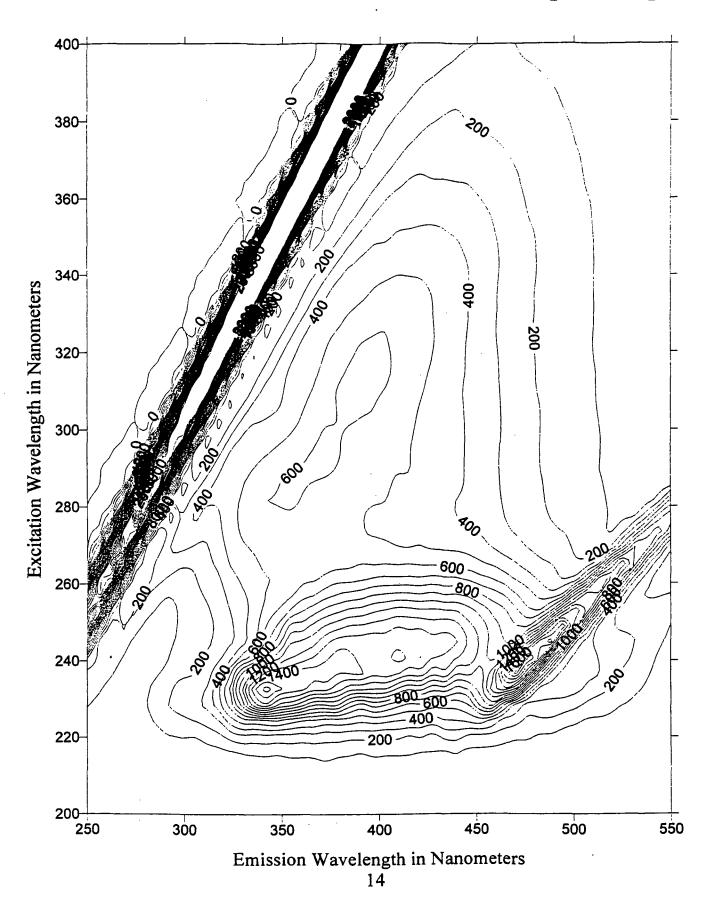


Figure 10
Fluorescence Contour Plot of a Typical Sawmill Leachate

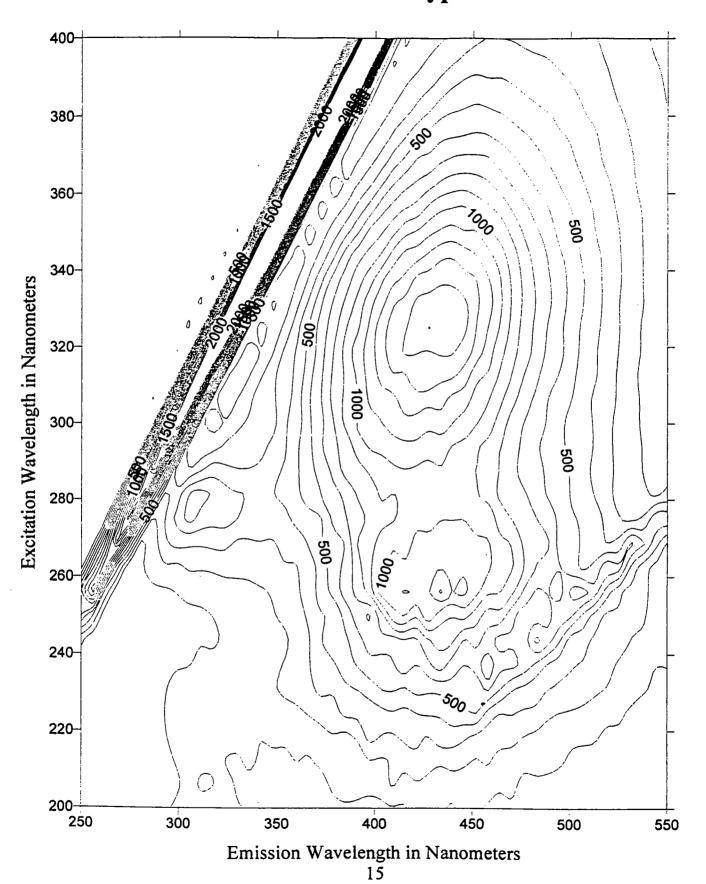


Figure 11
Fluorescence Contour Plot of a Typical Sewage Effluent

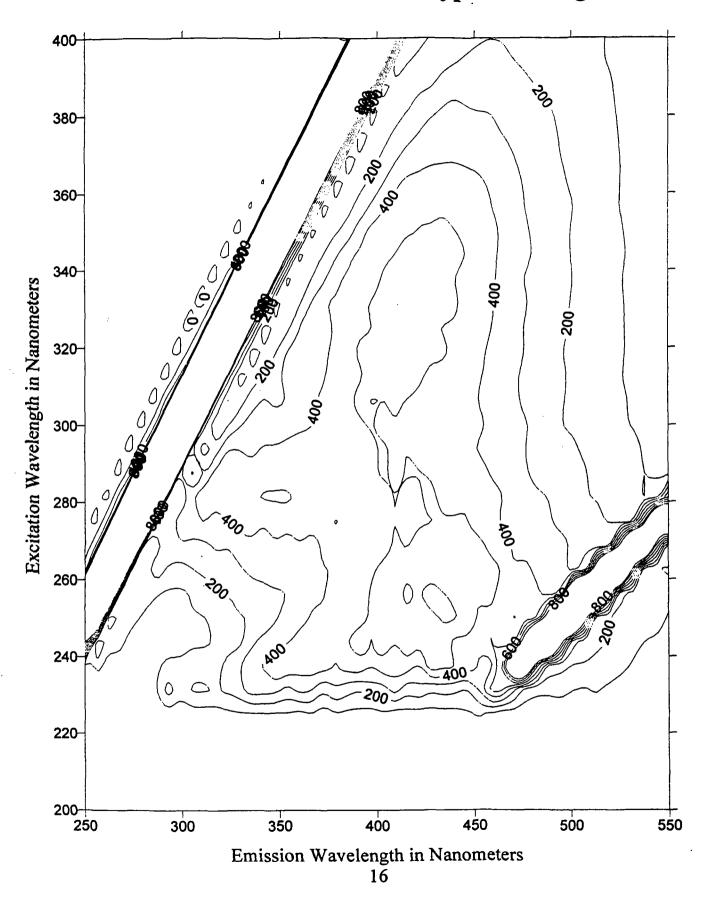


Figure 12
Zones A through D (Fluorescent Contour Plots)

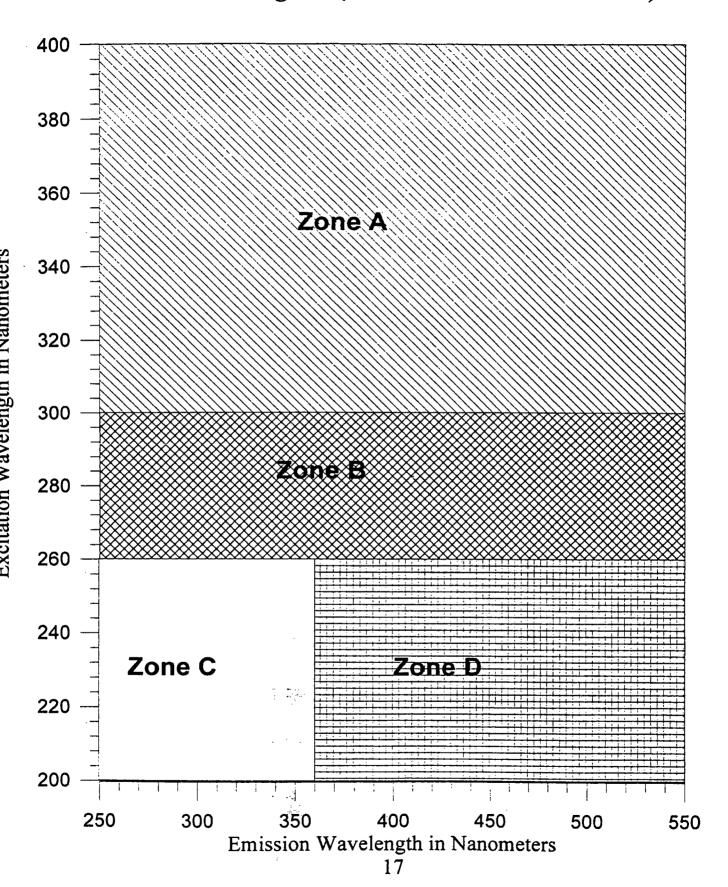
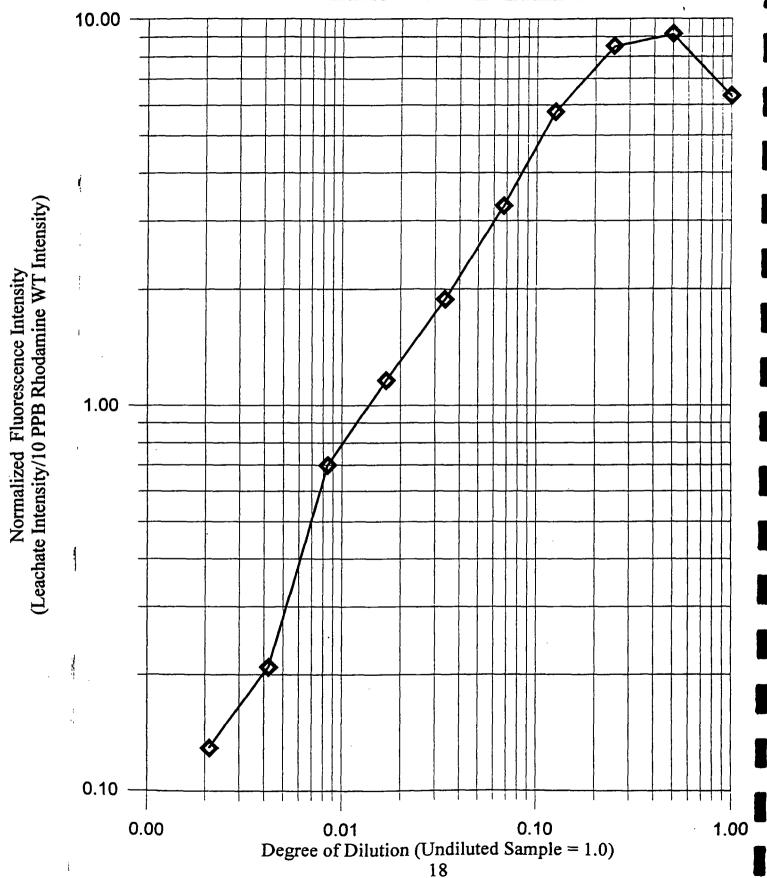


Figure 13
Normalized Fluorescence Intensity of B Zone Peaks
from Various Dilutions of a Landfill Leachate



The leachate analyzed displayed significantly more fluorescence than unimpacted water even when the leachate was diluted up to 100 fold. Fluorescence of undiluted leachate may be reduced somewhat due to inner-filter effects. Background waters typically exhibit peaks in the A, C, and D zones, but at significantly lower fluorescence intensities.

WET CHEMISTRY COMPARISON WITH FLUORESCENCE METHODS

Water samples were collected at six solid-waste disposal facilities and analyzed for leachate indicators using traditional wet chemistry techniques as well as both fluorescent techniques described above. The intent was to sample different types of water in the vicinity of each landfill. Sample locations were chosen to represent: leachate, leachate impacted water, potentially impacted water, and background water. The landfills selected for this part of the study included: Renfro's in Stone County near Branson West, Generally Hauling Sanitary Landfill near St. Clair in Franklin County, Superior Oak Ridge near Valley Park in St. Louis County, JZ Disposal Inc. near Wright City in Warren County, Southeast Sanitary Landfill near Kansas City in Jackson County, and Maryville Sanitary Landfill in Nodaway County.

GEOHYDROLOGIC SETTINGS

The first three landfills (Renfro's, Generally Hauling, and Superior Oak Ridge) were chosen to represent carbonate bedrock terrane of the Ozarks. Deeply-weathered surficial materials composed largely of the insoluble residues that remain after carbonate bedrock has been removed by solution-related activity characterize these facilities. The soils contain high percentages of rock fragments--mostly broken chert and sandstone beds. Clays in these soils are highly structured. The overall effect is that these surficial materials usually display relatively high permeability even after they have been compacted. A small portion of the Superior Oak Ridge facility has been lined with a flexible membrane liner, but the majority of all three landfills were

designed to rely on natural materials to isolate leachate from the environment. Each landfill has at least some major portion that has ineffective leachate collection or leachate collection of questionable effectiveness. These facilities would be considered the greatest risk to groundwater from a geohydrologic perspective of the six monitored because of permeable soils and karst bedrock which may allow rapid migration of fluids into shallow groundwater supplies.

Adsorption and filtration of landfill contaminants would be expected to be minimal.

Southeast Sanitary Landfill was chosen to represent an alluvial setting. This facility is underlain at depth by sand and gravel deposits of the Blue River. Locally silt and clay overbank deposits are present but coarse-grained materials predominate. The water table is shallow--within several feet of the ground surface on the west-side of the landfill and up to about 30 feet below the ground surface on the east side (river side) of the landfill. A portion of the facility has a flexible membrane liner but the majority of the footprint is essentially unlined with no leachate collection. Portions of the fill reportedly intersected the water table. Adsorption is limited in this setting but filtration is expected to be quite effective. Dilution of contaminants by large quantities of groundwater present here could reduce numerous contaminants to concentrations below action levels. Another potentially complicating issue is that this facility is located in an industrial area where other sources of contamination may be difficult to distinguish from those related to the landfill.

JZ Disposal was chosen to represent clay-rich glacial till over a buried preglacial channel sand. There are actually two different landfills at this location-a domestic waste landfill and a demolition waste landfill. Both facilities were essentially valley-fill operations that occupy adjacent south-north trending tributaries to Indian Camp Creek, which is located immediately north of both facilities. The uppermost surficial materials on the ridge tops surrounding the filled valleys are composed of silty and sandy clay till. Bedded silt, sand, and gravel deposits of preglacial origin are present beneath the till.

The preglacial channel is a useable aquifer with good yields and good water quality. Static water levels in the preglacial channel sand aquifer vary from essentially 0 adjacent to Indian Camp

Creek, north of the landfill, to about 100 feet below the ridge top south of the landfill.

Reportedly wastes were placed directly above the preglacial aquifer with no liner whatsoever.

Leachate collection via a perimeter drain is present at a portion of the facility but the placement of the drain suggests that it is only partially effective. Dilution of contaminants by large quantities of natural groundwater may occur at this location due to large amounts of groundwater present in the preglacial channel. This type of deposit is frequently used for public water supply in northern Missouri. Filtration of filterable contaminants would be expected to be high.

Maryville Sanitary Landfill is located above clay-rich glacial till. Locally, pockets of sand are present within the till that have been tapped as sources of groundwater for monitoring wells around the landfill. While the facility is not artificially lined, an abundance of plastic clay is available on-site, which was used to construct a compacted clay liner. Static water levels in monitoring wells vary from about 10 to 40 feet below the ground surface depending on the topographic position of the specific well. This geologic setting would be expected to allow the least migration of contaminants associated with leachate. Adsorption and filtration should both be relatively effective in retarding some contaminants while slow water movement should not allow rapid recharge or off-site migration unless macropores such as joints in the till allow the clay matrix to be circumvented. This facility also has a relatively well-designed leachate collection system.

METHODS

Using both the two-dimensional and three dimensional fluorescence spectrometer methodologies outlined above, 42 samples were analyzed and compared to wet chemistry analyses (Table 1). Using three dimensional data, fluorescent intensities of peaks in specific zones (A through D) of wavelengths were normalized as a ratio of the largest peak height in a given zone in comparison to the height of a 10 part per billion Rhodamine WT standard analyzed with a 17 nm synchronous scan. For instance, if a given sample had the same peak height in Zone A as the appropriate standard, the corresponding value for Zone A in Table 1 would be 1.0. Synchronous

TABLE 1

FLUORESCENT INTENSITIES OF SELECTED PEAKS OF RAW WATER SAMPLES

Landfill and Sample Location	Sample Number	A Zone	B Zone	C Zone	D Zone	2D	Wet Chem	Fluoresc LER
		3D	3D	3D	3D		Class	
Renfro's Gas Well #4 (Leachate)	98-2627	8.45	7.89	8.59	4.27	1.67	L	1.0
Renfro's West Wall Spring	98-2629	0.81	0.78	0.70	0.90	0.25	L?	0.4
Renfro's East Wall Spring	98-2631	1.11		0.48	10.1	0.19	BG	0.4
Renfro's Outfall 001	98-2633	0.60			0.57	0.17	BG	0.0
Renfro's MW 11	98-2623		0.30	0.30		0.19	BG	0.0
Renfro's MW 16A	98-2625		0.30*	0.30*		0.35*	ВG	0.2*
Renfro's North Eastwood Spring (Background)	98-2635			0.07	0.09	0.21	BG	0.0
Renfro's South Eastwood Spring (Background)	98-2637				0.09	0.21	ВG	0.0
Generally Hauling Leachate Outbreak (Leachate)	98-1616	3.00	227	227	237	0.77	L	1.0
Generally Hauling Leachate DS Outbreak (Leachate)	98-1610	4.59 p	309	485	393	1.15	Ĺ	0.1
Generally Hauling Landfill Spring	98-1612	0.75	0.81	122	0.84	0.26	L	0.6
Generally Hauling Piezometer 3	98-1614			0.13		0.24	ВG	0.0
Generally Hauling Piezometer 4	98-1618		0.13	0.18		0.23	ВG	0.0
Generally Hauling Cove Spring (Background)	98-1620	0.46		0.25	0.46	0.27	ВG	0.1
Superior Oak Ridge Leachate Tank (Leachate)	98-1628	4.93	9.12	4	2.10	7.75	L	1.0
Superior Oak Ridge Culvert Outbreak (Leachate)	98-1626	4,26	2.78 :	0.55	2.77	1.00	L	0.8
Superior Oak Ridge Sediment Pond	98-1624	1.72	1.74	1.15	1.59	0.38	L	1.0
Superior Oak Ridge Brown Spring	98-1634	4.19	1.90	3 .5 7	3.45	0.89	L	1.0
Superior Oak Ridge Brown Spring DS	98-1636	3.16		1.73	2.77	0.65	L?	0.8
Superior Oak Ridge MW 1117	98-1630		0.06	0.06		0.19	L?	0.0
Superior Oak Ridge Keifer Creek Spring (Background)	98-1638	0.18			0.24	0.17	L?	0.0
Superior Oak Ridge Castlewood Spring (Background)	98-1632	0.27	0.30	0.20		0.19	BG	0.0

Table 1 (Continued)

Landfill and Sample Location	Sample Number	A Zone 3D	B Zone 3D	C Zone 3D	D Zone 3D	2D	Wet Chem Class	Fluoresc LER
JZ Disposal Outbreak (Background)	98-2613	10.50	7 33	7.74	5.21	2.24	L	1.0
JZ Disposal Bluff Spring	98-2611	0.25			0.40	0.17	ВG	0.0
JZ Disposal, Well D	98-2607	0.53			0.47	0.22	BG	0.0
JZ Disposal, Well C	98-2605	0.35			0.55	0.21	L?	0.0
JZ Disposal, Well B	98-2603	1.57		1.04	1.05	0.33	L?	0.8
JZ Disposal, Well A (Background)	98-2601	0.16			0.33	0.19	BG	0.0
JZ Disposal Indian Camp Creek (Background)	98-2609	0.35			0.48	0.20	BG	0.0
SE Sanitary Landfill Leachate Sump (Leachate)	98-3298	437	2.26	237	3.12	0.88	L	1.0
SE Sanitary Landfill Well S3	98-3286	2.18	2.13	0.08	1.93	0.54	L?	0.8
SE Sanitary Landfill Well S5	98-3304	0.85	0.96	138	136	0.25	L?	0.7
SE Sanitary Landfill Well S7	98-3302	0.77	0.72	1,48	1.32	0.25	L?	0.7
SE Sanitary Landfill Well S1	98-3300	0.76	0.82		0.84	0.23	L?	0.3
SE Sanitary Landfill Blue River (Background)	98-3293	0.54	0.67	0.62	0.81	030	L?	0.3
Maryville Sanitary Landfill Manhole (Leachate)	98-3310	8.24	5.0T .=	4.25	5.87	1.29	L	1.0
Maryville Sanitary Landfill Battery Pit (Leachate)	98-3318		4.06	11.91	_	0.58	L	0.6
Maryville Sanitary Landfill MW-0207	98-3316		0.12	0.19		0.24	ВG	0.0
Maryville Sanitary Landfill MW-0205	98-3314				0.06	0.22	BG	0.0
Maryville Sanitary Landfill MW-0206	98-3320		0.41	0.51		0.48	BG	0.2
Maryville Sanitary Landfill MW-0204	98-3312	0.14			0.16	0.24	BG	0.0
Maryville Sanitary Landfill MW-0201 (Background)	98-2657			0.14		0.24	BG	00
Maryville Sanitary Landfill North Creek (Background)	98-3308	0.82	0.46		0.79	0.24	BG	0.2

^{*} Sample had high turbidity to the degree that it interfered with fluorescence.

scan results were also normalized to a 10 part per billion Rhodamine WT standard using a similar calculation utilizing only the largest peak for the sample analyzed. In specific leachate samples, dilution was necessary to reduce inner filter effects. In these instances only the largest fluorescent peak in a given zone or scan, out of all the dilutions analyzed, was used.

Summaries of these normalized results along with other pertinent information are listed in Table 1. The samples were then ranked for fluorescent intensities in each zone as follows:

Fluorescence contouring (three dimensional data) that displayed peaks in Zones A through D with normalized fluorescent intensities of 1.0 or more were assigned a numerical value of 0.2.

Intensities of 0.75 or more but less than 1.0 were assigned a numerical value of 0.1.

Synchronous scans (two dimensional data) with peak intensities of 0.3 or more were each assigned a numerical value of 0.2. Two-dimensional peaks with normalized intensities of 0.25 but less than 0.3 were assigned a numerical ranking of 0.1 for that factor. The numerical cutoffs listed above (1.0 and 0.75 for three-dimensional peaks and 0.3 and 0.25 for two-dimensional peaks) are based on observed fluorescent intensities of samples analyzed in the earlier phase of the study. In evaluating waters that are known to contain leachate and waters that are known not to contain leachate, it was observed that these cutoffs were exceeded only when leachate was present or when other organic sources were involved. The numerical values for all factors (Zones A through D on the three dimensional scans and a single value for the two dimensional scans) were then added together to produce an overall fluorescent ranking of the sample.

Thus if all five indicators exceed the highest cutoff, the leachate equivalency rating (LER) would be 1.0 but if only one major exceedance occurred, the LER would be 0.2. These ratings were then compared with independent wet chemistry results to determine the overall effectiveness of the fluorescence methods. Actual wet chemistry data are shown in a separate flood grant report which is in preparation. A rating of "L" under the "Wet Chem Class" in Table 1 indicates that other analytical data have been interpreted to classify this sample as leachate or leachate-impacted. A ranking of "L?" indicates the sample is either leachate-impacted or impacted by some other source of contaminants. A ranking of "BG" indicates that there is no significant evidence of impact by wastes. Known leachate and known backgrounds were labeled in

parentheses under the heading of "Landfill and Sample Location":

COMPARISON RESULTS

The fluorescence techniques developed generally agreed with wet chemistry techniques. Fluorescence methods were effective in distinguishing leachate and leachate-affected surface waters from background waters at apparent dilution rates up to one hundred to one. Similar success was achieved in distinguishing leachate-affected groundwater from background water in karst aquifers.

Leachate-affected groundwater was not detected using fluorescence analysis in a glacial till setting at the Maryville Landfill. However, interpretation of wet chemistry data did not clearly detect the presence of leachate in groundwater samples at this site either. While some fluorescent indicators may have been retarded, removed, or changed chemically as they passed through glacial clays, wet chemistry showed no significant impact of leachate on groundwater at this site.

Significant fluorescence was observed in every monitoring well at the Southeast Sanitary

Landfill, including those previously thought to be upgradient from the facility. It should be
noted that waste at this landfill is mounded as much as 80 feet above the surrounding floodplain.

The elevation of leachate within the landfill is not known but is suspected to be at some
elevation above the floodplain. This means that there may be no upgradient wells on-site.

Additional data clearly indicate that the supposedly upgradient well S3 contains constituents
indicative of leachate as well as methane gas.

CONCLUSIONS

Out of a total of nine samples tested that were known to be leachate or leachate impacted prior to sample analyses, an average LER of 0.93 was recorded. Out of a total of ten samples known to

represent a nonleachate background, an average LER of 0.06 was recorded. This average includes three samples that are suspected to have some degree of sewage impact.

Based on the results above, an LER of 0.4 or higher was considered to be evidence of impact by organic leachate. An LER of 0.2 to 0.3 indicated questionable impact and samples with this rating appeared to have been impacted by diluted leachate or sewage. An LER of 0.0 to 0.1 indicates the sample is either not impacted or impacted only slightly by organics that are fluorescent.

Wet chemistry indicated a total of 12 samples were definitely leachate-impacted. The fluorescence LER system, proposed in the previous paragraph, agreed on all 12 of these samples with an average LER of 0.97. Wet Chemistry indicated a total of 11 samples were questionably impacted with leachate. Fluorescence indicated eight of these 11 were either leachate-impacted or questionably impacted with an average LER of 0.36 for all 11. A total of 20 samples were characterized by wet chemistry as backgrounds. Of these 20, fluorescence characterized 16 as backgrounds with an average LER of 0.06 for all 20.

The fluorescence method outlined here agreed with wet chemistry results in 20 out of 23 classifications of leachate or questionable leachate impact. This success rate presupposes that the wet chemistry interpretations were correct. In all of the three disagreements, limited proof of leachate impact was present. One example, Keifer Creek Spring, near Superior Oak Ridge, was originally chosen as a "background" site. The recharge area for this spring probably does not include the landfill in question but it likely does include numerous sources of contamination. In conclusion, fluorescence methods were remarkably successful given the inherent complexities of organic chemistry, geohydrology, waste disposal histories and landfill design.

SUGGESTIONS FOR ADDITIONAL STUDY

Several changes have been suggested to improve the fluorescent methodologies used in this study.

Changing to different sample containers such as volatile organic analysis (VOA) vials could improve results by assuring capture of volatiles that could be lost using polypropylene cups with polyethylene caps. A concern has also been expressed that the plastics used in the disposable containers could be incorporated into the samples, especially when the sample may contain corrosive material. Simple comparisons of split samples could be made to determine if significant differences occur between the two containers.

More complicated improvements would involve buffering of the raw water samples or other treatments such as filtering, centrifugation or constant temperature baths, to standardize such factors as pH, turbidity and temperature. Time constraints limited development of such standardization techniques during this study.

Obviously an ultimate goal of investigators wanting to further this type of effort would be to determine what specific fluorescent substances are being measured with this method. This goal was beyond the scope of this investigation, which largely focused on fluorescent materials as tracers instead of contaminants. Additional fluorescence data are needed from water samples relating to numerous types of waste streams. As the database is enlarged the techniques used will doubtless be improved and refined.

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